

## Assistance Agreement Quarterly Report Summary: 9<sup>th</sup> Quarter

**Date of Report:** April 12, 2002

**Agreement No:** R82806301

**Title:** **Baltimore Supersite: Highly Time and Size Resolved Concentrations of Urban PM<sub>2.5</sub> and its Constituents for Resolution of Sources and Immune Responses**

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**Institution:** Department of Chemistry and Biochemistry, University of Maryland, College Park, MD

**Research Category:** Particulate Matter Supersites Program

**Project Period:** January 15, 2000 to December 31, 2003

**Objectives of Research:** Our primary objectives are to i) provide an extended, ultra high-quality multivariate data set, with unprecedented temporal resolution, designed to take maximum advantage of advanced new factor analysis and state-of-the-art multivariate statistical techniques; ii) provide important information on the potential for health effects of particles from specific sources and generic types of sources, iii) provide large quantities of well characterized urban PM for retrospective chemical, physical, biologic analyses and toxicological testing, iv) provide sorely needed data on the sources and nature of organic aerosol presently unavailable for the region, v) provide support to existing exposure and epidemiologic studies to achieve enhanced evaluation of health outcome-pollutant and -source relationships, and vi) test the specific hypothesis listed in our proposal.

### STATUS

As described in our previous report, all measurements at the Baltimore Supersite were terminated on September 14<sup>th</sup>, when vandals entered and set fire to our two main air monitoring trailer platforms. Nearly all our instruments were either destroyed or rendered unusable by smoke damage. The trailers and most of the equipment, totaling more than \$367,867 was covered by the State of

Maryland Insurance fund. Owing to the attack and other developments at Clifton Park, it was imperative that the site be moved to a new, safe location, requiring installation of utility power and a security fence. The site has now been restored at Ponca St. and first became operational in February 2002. In this report we detail the status of instrument and equipment replacement and changes to the sampling scheme.

**New Site.** A new site, located in an MTA employee's parking lot at 299 Ponca St. was found. We met at various times with MTA personnel to negotiate site access and lease agreement. The MTA generously granted us a cost-free lease.



**Figure 1.** The new Baltimore Supersite is located at 299 Ponca St., a short distance from Johns Hopkins Bayview Hospital.

**Equipment Purchased.** Most of the damaged/destroyed items have been fixed or replaced. This includes all of the site computers, LAN, telephone, modems, and associated items; an R&P 8400N semicontinuous Nitrate Monitor, two University of Maryland High-Frequency Aerosol Slurry Samplers, a Thermo-Systems Aerodynamic Particle Sizer (APS), and Sequential Organic filter/PUF sampler. Items not owned by the University, notably, a Thermo Systems, Inc. (TSI) Scanning Mobility Particle Spectrometer (SMPS) belonging to EPA and an Ruprecht and Patashnik (R&P) Model 8400S Semicontinuous Sulfate Monitor, belonging to Suzanne Herring were not losses reimbursable by the Maryland Insurance Fund. These instruments were replaced as described, below. Pursuant to discussions with our Contract Administrators, we replaced our irreparable EC/OC instrument with a more expensive, Sunset Labs instrument for semicontinuous ED/OC, to provide improved collection efficiency and compatibility with the EPA's standard speciation method

for EC/OC and other Supersites. To replace the destroyed R&P Sulfate Monitor we built a Harvard-type Semicontinuous Sulfate Monitor from parts, using a sulfur dioxide monitor purchased for the project. Additionally, we purchased a model 3010 continuous Condensation Particle Counter, model 3080 Electrostatic Claddifier, inlet impactor, Model 3077 <sup>85</sup>Kr aerosol neutralizer, and software from TSI, to construct a new SMPS system. This was a cost savings over a completely new instrument (about \$74,000) as TSI was able to use an old mobility column purchased years ago using University funds awarded to the PI.

**Other Equipment Acquired.** The TEOM used at the Clifton Park Site belonged to the Maryland Department of Environment and could not be replaced by the MIF. Instead we installed a 30° TEOM on loan from Dr. Philip Hopke. The unit is to be returned to Professor Hopke during the last week in May, at which time MDE anticipates being able to provide us with their replacement instrument.

**CSAS.** One instrument, our aging Classical Scattering Aerosol Spectrometer (a forward scattering instrument) was damaged, but as its function is probably better achieved with the TSI APS, which measures particle concentrations as a function of size over the same size range, we decided to use project funds to offset other losses rather than repair/replace the CSAS.

**Field Site Trailer.** Owing to requirements of the new site and to improve security, we ordered a single, double long trailer to house the instruments. The new trailer (48' x 12') was upgraded from 10- to a 12-ft width to be able to accommodate three new instruments (a Berner Impactor for size distributions of PAH; a semicontinuous ammonia monitor, and semicontinuous GC for volatile organic compounds) to be provided by colleagues but not used, previously, at the Clifton Park site. Additionally, the new trailer was ordered with an improved heavy-duty door to provide for additional security. After delivery at the site, we hired a contractor to install a wooden platform on the entire roof surface, to allow installation of the DRUM impactor, Speciation and FRM monitors, Berner Impactor, and to service the inlets for the various instruments. The roof platform was another upgrade, deemed necessary, in part, because of the lack of ground space at the new site and, in part, based on our experience with the previous trailers.

**Site Preparation.** To install the trailers at the new site a new utility installation was required and a fence had to be installed. The former encompassed replacement of the then existing transformer with a 100KW unit (provided by BG&E) and installation of a 600 A 240 V service for our trailer and a 100 A 240 V service for MDE's trailer.

**Site Operation.** The trailer was installed during the latter part of January, 2002, owing to delays in securing a lease agreement with the MTA. Preliminary Data collection was initiated on February 19<sup>th</sup> with the Nitrate, Sulfate, APS, and SMPS instruments; Met, Feb 20<sup>th</sup>; and EC/OC, Feb 21<sup>st</sup>. The SEAS instruments were also started on Feb. 19<sup>th</sup>, however, training and problems with various components precluded valid sample collection until a few weeks later. The DRUM impactor, FRM Mass Monitor, two speciation monitors were installed on the roof during the month of January.

## **PROGRESS SUMMARY/ACCOMPLISHMENTS**

**SEAS.** A new control program was written, tested during the month of February, and installed at the Baltimore Supersite. The program improves ease of human interaction, provides enhanced diagnostic data output, and vastly improves user control of setup and calibration parameters. Additionally, operational procedures have been built into various control operations and are displayed on screens which are generated by the program for key operational sequences. The user is now prompted to perform various activities involving fraction collector setup, blanking filter installation, and other activities.

In addition to the new program, a new electronic control module was constructed and tested. The new module houses all of the critical electronic components (power supplies, valve driver relays, thermocouple signal conditioner, and I/O boards. The new module is designed to eliminate reliability problems associated with exposed wiring and components. The new module has been installed on the SEAS metals system at Ponca St.

Collections have been made continuously with both the SEAS cytokine and SEAS metals instruments at 30 minute intervals since March 30, 2002.

### **Cytokine Assays**

Work during this quarter concentrated on characterizing the response of the *in vitro* exposure assays under development to specific known components of PM<sub>2.5</sub> samples to determine the extent to which different endpoints might be specific for and correlate with different classes of chemicals.

**LPS content of SEAS PM<sub>2.5</sub> samples.** Because LPS is a well known stimulator of immune cells and has been reported to be present in PM samples, we assayed a series of SEAS samples collected from the FMC site in South Baltimore for LPS content. Analysis indicated that most of the SEAS samples collected every 30 min for a period of 30 hours contained LPS (measured by the *Limulus* assay) at concentrations ranging from 30-50 ng/ml, although during the 30 hr period LPS concentrations dropped as low as 3 ng/ml. It is not clear whether the LPS present in these samples is a natural component of the collected PM<sub>2.5</sub>, or whether it is a product of sample contamination during collection and storage. This is currently being investigated.

**A549 airway epithelial cell bioassay.** The response of A549 cells to SEAS particle exposure as measured by IL-8 and MCP-1 release was compared to determine whether there was a differential response between these two chemoattractant cytokines. Exposure of cells to a series of samples collected from the FMC Site showed that IL-8 release varied to a greater extent (6 fold) than MCP-1 release (1.7 fold) over a 12 hr time period. These results were consistent with evidence from experiments with specific stimulants of the cytokine responses. IL-8 release by A549 cells was much greater when the cells were exposed to ZnCl<sub>2</sub> than when the cells were exposed to LPS. On the other hand, MCP-1 release was stimulated by LPS, but not by ZnCl<sub>2</sub> exposure. These results suggest that measurements of IL-8 release will more closely reflect biologically active metals in the SEAS PM<sub>2.5</sub> samples, while MCP-1 release will be more dependent upon the LPS content of the samples.

**RAW264.7 macrophage cells.** Similar studies to those described above for the A549 cells were conducted with the RAW 264.7 macrophage cell line using the release of IL-6 and TNF<sub>α</sub> as endpoints. Results showed that ZnCl<sub>2</sub> exposure did not stimulate the release of either of these cytokines, however both were released in response to LPS exposure. The magnitude of the response of the RAW264.7 cells to LPS for the IL-6 cytokine was much more robust than the TNF<sub>α</sub> response. Experiments with polymixin B (an inhibitor of LPS) showed an inhibition of the IL-6 release by the RAW264.7 cells exposed to SEAS particles collected from the FMC Site, although to varying degrees, indicating that incorporation of polymixin B into the bioassay paradigm under development will be useful for dissecting out the response of the cells to different components of the SEAS PM<sub>2.5</sub> samples.

### **DRUM Impactor**

Drum Impactor measurements were initiated at Ponca st. on Feb. 28<sup>th</sup>. Three sets of 8-day samples were collected on the following dates: 2/28 - 3/7; 3/13-3/21; and 3/21-2/29.

### **Single Particle MS**

**Data Collection.** The data acquisition program for RSMS-3 automatically collects single particle mass spectra at regular intervals. For the sampling period between 3/20/02 and 3/23/02, a complete sample cycle was performed every three hours except for maintenance periods. During an individual sample cycle, measurements were made sequentially for 9 particle sizes. For each size, the measurement period ended after 10 minutes or the acquisition of 30 particle mass spectra, whichever came first. Typically, 60-70 minutes were required to cycle through the 9 particle sizes for the ambient particle concentrations present during this time period.

Table 1: Summary of Activities and Data Collection.

Date	Activity	Data Collection
1/1/02-3/13/02	Rebuild and test replacement single particle mass spectrometer.	None
3/14/02-3/19/02	Install single particle mass spectrometer in Baltimore and prepare for sampling.	None
3/20/02-3/23/02	Obtain ambient single particle spectra. During this period, each sample cycle consisted of measurements for 9 particle sizes between ca. 40 nm and 1000 nm. Up to 30 particle mass spectra were obtained for each size. The sampling cycle was repeated every 3 hours.	Spectra acquired during each 24 hour period:  3/20 – 680 particle spectra 3/21 – 1715 particle spectra 3/22 – 997 particle spectra 3/23 – 1547 particle spectra

**Data Analysis.** As Table 1 shows, 4939 particle spectra were obtained over the 3/20/02 to 3/23/02 time period. The particle number on 3/20/02 was significantly lower because data acquisition began in the middle of the day. We have not yet had a chance to validate, analyze and interpret this data in any detail. However, we have briefly looked at data for another day (3/25/02) and make the following preliminary observations about the Baltimore aerosol.

- Eleven particle classes were identified from a preliminary analysis of the 1676 particle spectra collected on 3/25/02. The striking feature of this data is the ubiquity of nitrate. Over 90% of the detected particles gave an appreciable signal from the nitrate marker ions, as expected during the cold periods since the ammonium nitrate equilibrium is highly temperature dependent.
- The main particle types observed on 3/25/02 were nitrate (70% of all detected particles), nitrate/organics (20% of all detected particles) and potassium/organics (8% of all detected particles). The remaining particles were divided among organics/soot (1%), and metals (1%). Metals observed are iron, sodium/potassium and copper.
- The relative numbers of particles in each class appeared to change significantly from one measurement period to the next. We have not yet had a chance to quantify these temporal variations or correlate them with other chemical, physical or meteorological data. Particle analysis rates were greatest in the ca. 100-200 nm aerodynamic diameter range, although particles were detected throughout the size range of the instrument (ca. 40-1000 nm). We have not yet had a chance to study the particle size characteristics of the various classes.

### Sequential Organic Compound Sampler

Our custom-built sequential organic filter/PUF sampler was designed to permit sequential sampling for up to 5 periods at flowrates up to 500 LPM or sequential sampling with 4 channels and simultaneous collection of a 24-hr sample at 100 LPM. The unit was fully assembled and installed in the Ponca St. Trailer for testing in January, but was found to suffer from faulty workmanship. The system was totally disassembled and inspected. We found improper thread installations which have created serious leaks, and parts glued together that were to have been welded. All of the fittings have now been replaced, the main PUF enclosures have been disassembled and properly welded. The unit should be leak tested by April 15<sup>th</sup>.

**SMPS/APS.** As mentioned above, the SMPS and APS instruments were brought online on February 19<sup>th</sup>, 2002. Each instrument records aerosol a (roughly) 5 min average aerosol particle spectrum every 5 minutes. Data capture efficiency for these instruments - expressed as number of 5 minute periods for which valid spectra were collected divided by the number of possible 5 minute data collection periods, was 99% or greater, each, in February, March, and April.

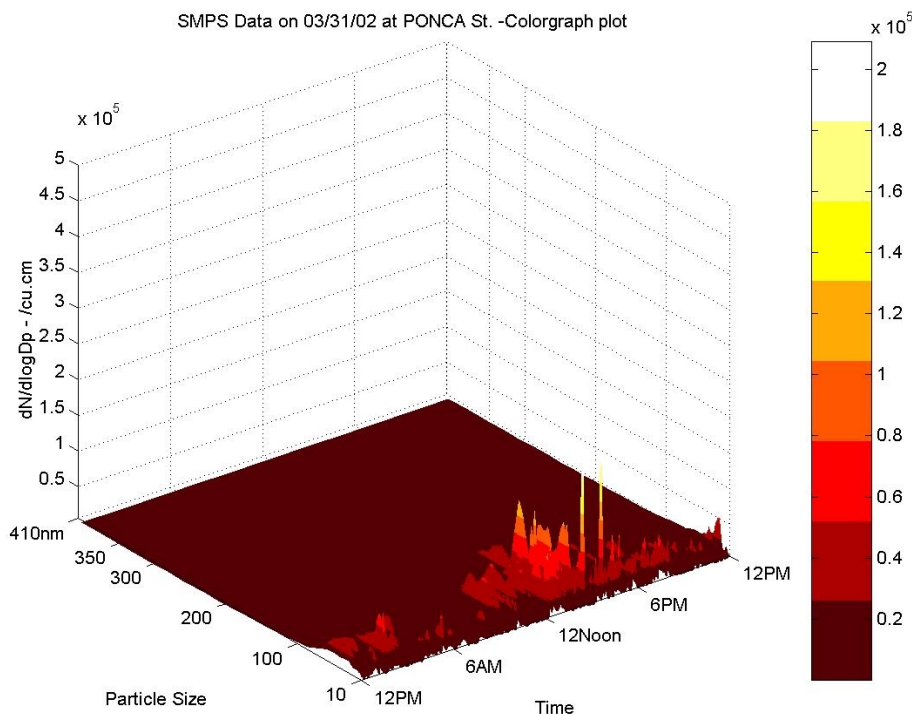


Figure 2. Nucleation events are evident in SMPS data of March 31, 2002

### Ultra-High-Volume Aerosol Sampler

The new 15-filter cassette box, installed inside the trailer by NIST, has been tested. This unit and the old 10-filter cassette box were installed inside the trailer and have undergone testing. It appears that ambient indoor trailer temperature is insufficient to prevent water from condensing on the filters during high relative humidity conditions. As these conditions occur with substantial frequency, the filter cassettes are being moved to the roof, where solar heating has

been adequate to prevent condensation most of the time. A computer control program has been designed and will be coded in visual basic in January, 2002.

### **Preliminary Data Analysis**

Principle component analysis (PCA) was performed on the 4.5-day data set collected at Clifton Park from September 6<sup>th</sup> - 10<sup>th</sup>, 2001. The main objectives of this work were to identify the probable source types of PM pollutant measured at Clifton park, Maryland, to investigate the difference between classical PCA) results obtained from different time-resolved (30-minute and 1-hr) chemical data, and to establish a fundamental database to be used in comparison with results of Positive Matrix Factorization (PMF2) analysis using the same measurement data in the near future work. The work focused on only the identification of the source types of highly time-resolved PM data measured at the site.

Highly time-resolved SEAS, nitrate, sulfate, carbonaceous species (OC and EC), and meteorological parameters (wind direction, wind speed, ambient temperature, and relative humidity) were used in the present data analysis. 30-minute integrated SEAS samples were collected during five-day sampling periods in September 2001, and then analyzed for trace elements by GFAAS. Nitrate, sulfate, and meteorological data were monitored on a 10-minute time interval, and averaged over a 30-min period to conduct the statistical analyses along with 30-min integrated SEAS data. Organic and elemental carbons (OC and EC) concentrations were recorded by R&P 5400 carbon analyzer on a 1-hr time interval. In order to see the influence of 1-hr averaged aerosol data on the source categories extracted, all chemical data including SEAS were averaged over 1-hr period.

There were some missing and below-detection limit data in the Clifton SEAS data. Missing data pose problems for factor analysis because the statistical software requires complete matrices. To deal with missing values, one can delete the samples that contain them, or substitute estimated concentrations such as means. Missing data in this preliminary work were replaced with mean values of their elements as suggested by Huang et al. (1999). They mentioned that mean substitution appeared to be the preferred method for handling missing values.

Three kinds of PCA analyses were performed; Firstly the PCA was undertaken with only the 30-minute SEAS data. Secondly it was carried out with combined data of 30-min. SEAS, nitrate, sulfate, and meteorological parameters. Lastly 1-hr averaged data were used for the PCA analysis. The analyses were performed using SPSS software version 10.0.

**Results and discussion.** In this progress report, the results of PCA analysis for the 1-hr averaged chemical data were described. However the results from the other two cases (PCA1 and PCA2 files) were similar to those obtained from the 1-hr data. Only those factors with a variance greater than 1.0 after VARIMAX rotation were retained. As seen in PCA3 file, eight factors were retained, and they explained ~87% of the total variance of the data set. The first principal component (PC) is loaded with Cd, Mn, Pb, and Zn, representing incineration emissions. The second PC is associated with meteorology, with absolute high loadings for wind speed, temperature, and relative humidity. From the time series data, it is apparent that elevated plumes, e.g., those from the coal & oil fired power plants, and steel mill/road dust sources are mainly observed during the daytime, i.e., after the morning inversion disperses and the surface wind speed increases. Under low wind speeds associated with the morning and evening hours, elevated plumes either don't mix down, or are more isotopically dispersed and thus diluted more. Clearly, road dust will tend to be observed at higher concentrations when winds are strong

enough to transport the material. Thus, there is some loading of the dust and power plant signals on this factor. The third PC has high loadings for  $\text{NO}_3^-$ , OC and EC, representing the motor vehicles emissions. Grouped with carbon particles, secondary nitrate is most likely to be formed in the atmosphere from nitrogen oxides directly emitted from the motor vehicles. The relationship between them is well described in ECOC and  $\text{NO}_3$ . The PC4 correlates well with Ni, Se, and Al, representing the oil and coal fired power plants emissions. Inspection of the time series data suggests that these are result from the influence of the Brandon Shores and Wagner power plants, which lie about 160 degrees, i.e., to the southsouth east of the site. The PC5, with high factor loading for Cu, Mn, and Pb, is likely to be emitted from steel meel operation. The PC6 is highly loaded with  $\text{SO}_4$ , secondary sulfate particles. As and wind direction components are associated with the PC7 and PC8, respectively, indicating unexplained ones. In this preliminary work, PCA were performed with several data conditions, 30-min and 1-hr data. The results obtained will be used as supplementary data in comparison with PMF results in the near future work.

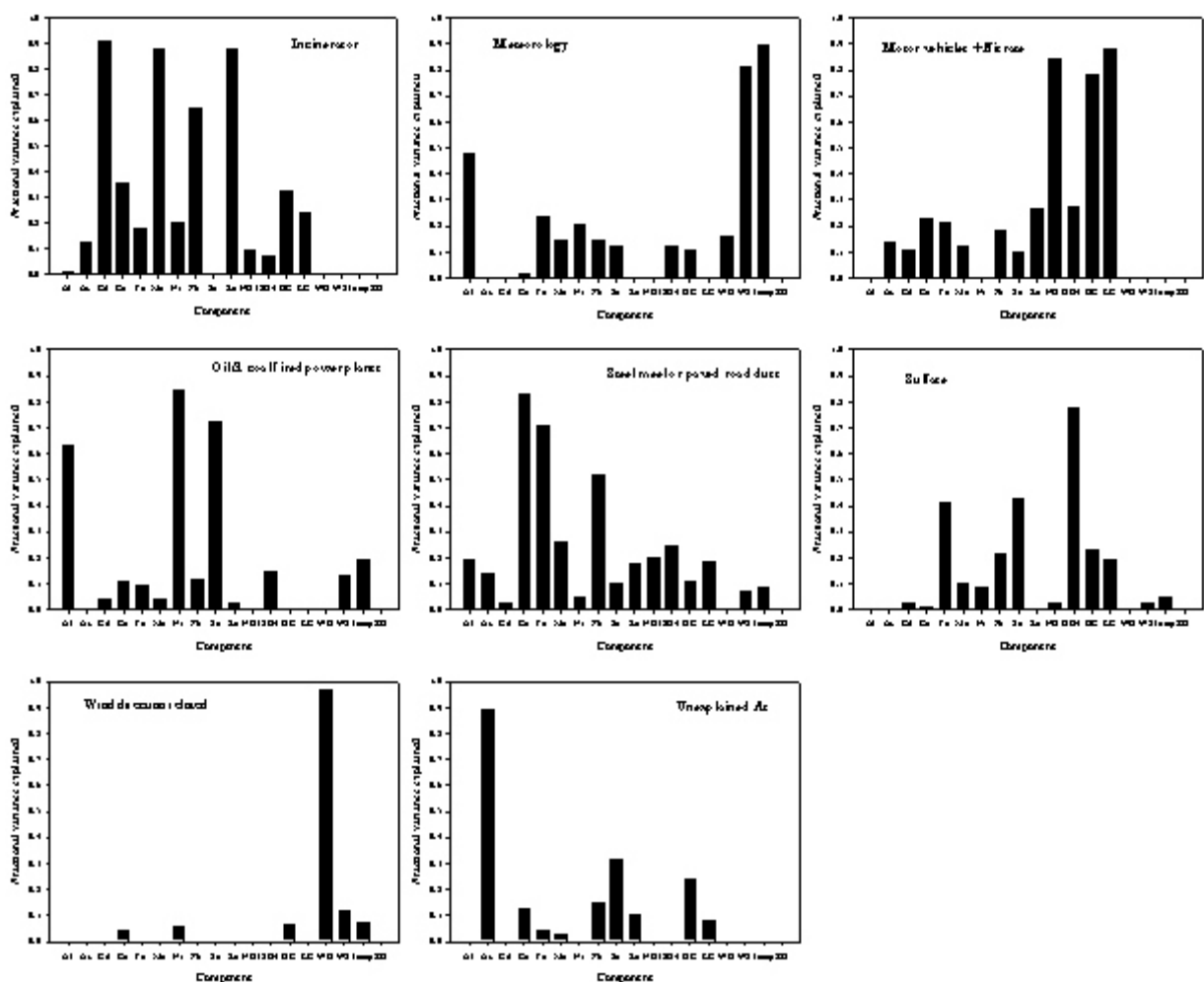


Figure 3. PCA results for Clifton Park data of September 6-10, 2001 reveal power plant, steel, incinerator, dust, motor vehicle, and a secondary sulfate factors.



## **Website**

Our Static Web site ([www.chem.umd.edu/supersite](http://www.chem.umd.edu/supersite)) was extensively revised by our new webmaster, Dr. J. Patrick Pancras. It contains color maps of the Baltimore Region prepared previously in ARCVIEW, and maps showing major PM emission sources (obtained from the EPA AIRS data base), metals emission sources (TRI data), and estimates of emissions as well as the location of our sampling sites and key streets, the efficiency curve for the UMCP all glass inlet impactor; SEAS data taken at College Park, MD, showing resolution of sources; and a 2-D scan showing relative particle concentration data showing traffic pollution over Baltimore streets. Current versions of all SOPs are also available on the web site. Recently, we've added pictures of the new Ponca St. Site as well as SEAS data derived from 30 min measurements made at the Clifton in September 2001 (click on "Key Instruments").

## **Publications/Presentations/meetings**

Ondov, J. M. (2002). Unprecedented Source Apportionment with the University of Maryland Semi-Continuous Elements in Aerosol System Presented at the Regional AQ Modeling & Data Analysis Meeting, sponsored by MARAMA, OTC, NESCAUM and MANE-VU, January 23-24, 2002, Baltimore, MD.

Ondov, J. M. (2002). Highlights of the Baltimore Supersite Project: A New Paradigm for Management of Toxic Emissions. Seminar presented at the Quarterly MDE/UMD meeting, February 15, 2002, UMCP.

Ondov, J. M., Kidwell, C. B., Catino, D. H., Moore, J., Chang, Y. C., Pancras, J. P., Park, S. S. (2002). Resolution of Contributions of Primary Particle Constituents from Individual Power Plants with SEAS. Presented at the US DOE and National Energy Technology Laboratory conference, "PM2.5 and Electric Power Generation: Recent Findings and Implications," April 9-10, Pittsburgh, PA.

## **Future Activities.**

1. We will continue to hold weekly PI teleconferences as needed.
2. SEAS: Tests have been devised to i) ascertain the optimal storage procedure for samples collected for cytokine assays, ii) determine intercomparability of colocated SEAS instrument; and to determine collection efficiency relative to an integrated filter based method with an identical (PM1.25 inlet).
3. Database: Project data will continue to be imported into the Baltimore Supersite Relational Data base.
4. The Sequential Organic Sampler will be laboratory cleaned, reassembled at Ponca St., and the system operated for performance testing in the next two weeks. Preliminary sampling will be conducted. We will probably perform preliminary collections until approximately 20 samples representing various wind directions are collected. Full scale intensives will be conducted in July and November, 2002.

